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TITLE : NONAQUEOUS ELECTROLYTE FOR BATTERY AND NONAQUEOUS ELECTROLYTE BATTERY

ABSTRACT : PROBLEM TO BE SOLVED: To effectively prevent an evil influence by a halogen acid, and prevent the degradation of a battery, an electrolyte and a battery can material or the like by adding an inactive complex forming compound to a nonaqueous electrolyte containing a support electrolyte capable of generating a halogen acid by reacting with water so as to interact with water and the support electrolyte.

SOLUTION: Representative one of a complex forming compound as a compound which is added to a nonaqueous electrolyte and forms an inactive complex by interacting with water and a support electrolyte, is a carbodiimide compound. When there is no carbodiimide compound, a PF_6 anion generated by ion dissociation of LiPF_6 isolates HF by reacting with water, but when the carbodiimide compound exists, a double bond part of a diimide bond part ($-\text{N}=\text{C}=\text{N}-$) weakly makes a hydrogen-bond with a water molecule, and since a complex where a PF_6 anion electrically bonds to these is formed, HF is not generated. An adding method of the complex forming compound is not particularly limited.

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JAPANESE

[JP,10-294129,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] Nonaqueous electrolyte for cells characterized by adding a complexing compound which does not produce halogen acid by interacting with said water and supporting electrolyte to nonaqueous electrolyte containing a supporting electrolyte which reacts with water and may produce halogen acid, and forming an inactive complex in it.

[Claim 2] A nonaqueous electrolyte cell characterized by using nonaqueous electrolyte for cells according to claim 1 as an active material of either positive/negative electrode at least, including a lithium or its compound.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the nonaqueous electrolyte for cells which took the cure of originating in a small amount of moisture which may intervene unescapable about the nonaqueous electrolyte for cells, and a nonaqueous electrolyte cell in the lithium secondary battery using the nonaqueous electrolyte which used the fixed halogenated compound etc. as the supporting electrolyte in more detail etc., and halogen acid being generated, and the nonaqueous electrolyte cell using this.

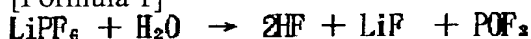
[0002]

[Description of the Prior Art] A lithium or its compound is used for an electrode active material, and the nonaqueous electrolyte cell using the organic solvent which contains a supporting electrolyte as the electrolytic solution from that attracts attention in the usefulness as the rechargeable battery turned to the primary cell as for example, a small power supply for electronic parts, and the dc-batteries of an electric vehicle, or a lithium ion battery.

[0003] in these nonaqueous electrolyte cells, it is a halogenated compound at the above-mentioned supporting electrolyte LiPF₆ etc. -- although used well, if some moisture is mixing unescapable into the electrolytic solution which must be non-water or the moisture produced by adsorption from other cell materials exists, a reaction as shown in the next "*** 1" will occur, and the halogen acid like hydrogen fluoride HF will be generated.

[0004]

[Formula 1]



[0005] Hydrogen fluoride has the problem referred to as degrading a cell component and degrading the cell engine performance further. Furthermore, it is known that the reaction of the above "*** 1" will be promoted by the pyrosphere. For this reason, for example, it especially sets to the rechargeable battery for dc-batteries of the electric vehicle with which stable actuation in the temperature region of -30-degreeC-60-degreeC is demanded, and a problem is a remarkable next door and LiPF₆. It is supposed that the nonaqueous electrolyte cell used as a supporting electrolyte is difficult to apply.

[0006] And in order to solve this problem, the following proposals are made conventionally. for example, it sets to invention of the nonaqueous electrolyte rechargeable battery indicated by JP,4-284372,A -- LiPF₆ the nonaqueous electrolyte used as a supporting electrolyte -- receiving -- aluminum 2O₃ MgO and BaO from -- by adding the oxide chosen, these oxides adsorb the hydrogen fluoride produced in the electrolytic solution, and it is supposed that it will remove out of the system of reaction.

[0007] Moreover, it is LiPF₆ if it sets to invention of the nonaqueous electrolyte cell indicated by JP,7-122297,A. It is supposed by adding an acid anhydride (for example, acetic anhydride) that these acid anhydrides catch the water in the electrolytic solution beforehand, and will control the reaction of the above "*** 1" to the nonaqueous electrolyte used as a supporting electrolyte.

[0008]

[Problem(s) to be Solved by the Invention] However, about invention given in said JP,4-284372,A, according to this artificer's supplementary examination, since removal of hydrogen fluoride advances very slowly depending on the oxide of the addition which can be actually permitted as a cell, it does not fulfill the generating speed of hydrogen

fluoride. Therefore, there is a problem said for not coming to prevent deterioration of the cell by hydrogen fluoride etc. effectively.

[0009] On the other hand, although the dehydration effect by the acid anhydride is high about invention given in said JP,7-122297,A consequently, the acid resulting from an acid anhydride will be generated and, so to speak, it is only what replaces halogen acid by other acids. And as opposed to halogen acid, although an acetic acid etc. is weak acid relatively, there is no change in bringing about deterioration of the electrolytic solution and a cell can material too, and it has not become essential solution to it.

[0010] So, in this invention, in the nonaqueous electrolyte containing the supporting electrolyte which reacts with water and may produce halogen acid for cells, or the nonaqueous electrolyte cell using this, the evil by halogen acid is prevented effectively and let it be the technical technical problem which should be solved not to produce a secondary problem like the above-mentioned conventional technology moreover, either.

[0011]

[Focus] This artificer perceived that it was effective in solution of the above-mentioned technical problem to confine the moisture leading to [of halogen acid] generating by the harmless complexing reaction with a large reaction rate.

[0012]

[Means for Solving the Problem]

[0013] (Configuration of the 1st invention) A configuration of the 1st invention (invention according to claim 1) of this application for solving the above-mentioned technical problem is nonaqueous electrolyte for cells which added a complexing compound which does not produce halogen acid by interacting with said water and supporting electrolyte to nonaqueous electrolyte containing a supporting electrolyte which reacts with water and may produce halogen acid, and forming an inactive complex in it.

[0014] (Configuration of the 2nd invention) A configuration of the 2nd invention (invention according to claim 2) of this application for solving the above-mentioned technical problem is a nonaqueous electrolyte cell using [including a lithium or its compound] nonaqueous electrolyte for cells according to claim 1 as an active material of either positive/negative electrode at least.

[0015]

[Function and Effect of the Invention] In the 1st invention and the 2nd invention, even if some moisture is mixing into nonaqueous electrolyte or the moisture produced by adsorption from other cell materials exists, these moisture is confined by the complexing compound into an inactive complex.

[0016] Unlike generation of the halogen acid which is static reaction, generally, since a complexing reaction has strong irreversibility, rather than the reaction of the above "*** 1", a complexing reaction gives priority to it and it occurs. For this reason, generation of halogen acid is prevented effectively.

[0017] And since the reaction rate is quick as a general feature of a complexing reaction, there is no fault by lack of a reaction rate like invention of a publication in JP,4-284372,A, and there is also no fault referred to as producing other harmful matter secondarily like invention of a publication in JP,7-122297,A in this invention.

[0018] In spite of using the supporting electrolyte which reacts with water and may produce halogen acid from the above thing in the nonaqueous electrolyte for cells or the nonaqueous electrolyte cell concerning this invention, even if water mixes in nonaqueous electrolyte, deterioration of a cell component and deterioration of the cell engine performance are prevented.

[0019]

[Embodiment of the Invention] Next, the gestalt of implementation of the 1st invention and the 2nd invention is explained.

[0020] [Object of 1. this invention] All the nonaqueous electrolyte cells using the nonaqueous electrolyte for cells and this containing the supporting electrolyte which reacts with water and may produce halogen acid in principle can be set as the object of this invention. Now, the so-called "lithium cell" with which a lithium or its compound is used for a nonaqueous electrolyte cell at least as an electrode active material of either positive/negative electrode occupies most.

[0021] While using occlusion and the carbon material which can be emitted for the lithium battery (rechargeable battery) and negative electrode which use activated carbon, 2 titanium sulfides, or molybdenum disulfide for a positive electrode while a lithium or its alloy is included in the lithium dry cell (primary cell) and negative electrode which use a manganese dioxide, zinc fluoride, copper oxide, or a thionyl chloride for a positive electrode as 2 of such

a lithium cell that is the object of this invention, and an example of 3 while using a lithium for a negative electrode for a lithium ion, the lithium ion battery which uses a lithium transition-metals compound for a positive electrode can be mentioned.

[0022] In addition, even if it is not the above lithium cells, as long as the technical problem of said this invention may arise, they are the nonaqueous electrolyte for object slack cells of this invention, and a nonaqueous electrolyte cell.

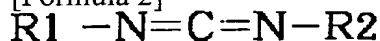
[0023] [2. supporting electrolyte] A supporting electrolyte means the material added in order to say that the conductivity of the electrolytic solution is raised and charge and discharge of a cell are performed efficiently in the nonaqueous electrolyte for cells. supporting electrolyte known well LiPF₆ LiBF₄ although it is, in this invention, it limits to these -- not having -- others -- for example, -- The general supporting electrolyte which reacts slightly with water and may produce halogen acid like hydrogen fluoride like LiAsF₆ is contained.

[0024] [Organic solvent in the nonaqueous electrolyte for 3. cells] As long as there is no mismatching special [with a supporting electrolyte], there is no limitation in the class of organic solvent. Ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate, dimethoxyethane, gamma-butyrolactone, etc. and two or more sorts of these mixed solvents can be used as the example of 2 and 3.

[0025] [4. complexing compound] The complexing compound of this invention says what reacts with water and said supporting electrolyte, and forms an inactive complex. The typical thing is a carbodiimide compound shown in the next "*** 2."

[0026]

[Formula 2]



[0027] the above "*** 2" -- setting -- R1 and R2 respectively -- a hydrogen atom or a hydrocarbon group -- being shown -- R1 R2 You may differ identically and mutually. The shape of a chain of saturation or partial saturation, the letter of branching, or an annular (aromatic series is included) hydrocarbon group is included with a "hydrocarbon group" here.

[0028] When the complexing compound of this invention is a carbodiimide compound shown in "*** 2", it is surmised that the complexing mechanism is as follows.

[0029] That is, it is LiPF₆ when there is no carbodiimide compound. Although the PF₆ anion produced by ionic dissociation reacts with water and separates HF like the above "*** 1", if a carbodiimide compound exists, the double bond section of diimide bond part-N=C=N- will carry out hydrogen bond to a water molecule weakly, and the complex which the PF₆ anion combined with them electrically will be formed, for this reason it will be thought that HF is not produced.

[0030] It sets in the above complexing mechanism and is R1 and R2. Although it does not participate in complexing directly, it has the work referred to as making formation of a complex easy by securing the solubility to the nonaqueous electrolyte of a carbodiimide compound. It is more desirable that this reason to a carbon number is the alkyl group or cycloalkyl radical of 3-8. There are the following as the example.

[0031] iso- [respectively as opposed to a straight chain-like propyl group butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, and these], sec-, and tert- etc. -- radical of all the structural isomers that have a relation.

[0032] A cyclohexyl radical, a methyl group (cyclohexyl), the methylcyclohexyl radical that has a methyl side chain in the substitute location of arbitration, the dimethyl cyclohexyl radical which has a methyl side chain in the substitute location of arbitration or (methyl) (cyclohexyl) a methyl group, the ethyl cyclohexyl radical which has an ethyl side chain in the substitute location of arbitration.

[0033] Moreover, R1 and R2 You may be the phenyl group of partial saturation, a naphthyl group, a vinyl group, etc., and may be the alkyl groups or cycloalkyl radicals other than a carbon number 3 - 8. Furthermore, it is R1 and R2. One side may be the alkyl group or cycloalkyl radical of carbon numbers 3-8, and another side may be the phenyl group of partial saturation, a naphthyl group, a vinyl group, etc. alkyl groups other than a carbon number 3 - 8 or a cycloalkyl radical, or a hydrogen atom.

[0034] These complexing compounds may use together two or more kinds of things, using the thing of a single class. Since a carbodiimide compound says that the moisture content in nonaqueous electrolyte is usually about 30 ppm, it is desirable to add more than 30 ppm to nonaqueous electrolyte weight. on the contrary, 10,000 ppm since it says that

the conductivity of the electrolytic solution itself is lowered the addition to exceed -- senselessness -- or it is not desirable.

[0035] There is no limitation in the method of adding the complexing compound of above this inventions, for example, it may add to nonaqueous electrolyte before cell assembly, or you may add directly in a cell container before **** after cell assembly. Special limitation will be in the distributed condition of the complexing compound added to nonaqueous electrolyte.

[0036] [the positive electrode of 5. nonaqueous electrolyte cell] -- the configuration of a positive electrode is [that there is no limitation in any way] well-known unless it is contradictory to the principal part of the configuration of this invention, since it is not the principal part of the configuration of this invention -- it is -- it is -- the configuration of arbitration is employable.

[0037] the case where for example, a nonaqueous electrolyte cell is a lithium ion battery -- as the active material of a positive electrode -- LiCoO_2 , LiNiO_2 , and LiMn_2O_4 etc., at least, the mixture which made a kind, and an electric conduction assistant and a binder the shape of a paste with the partially aromatic solvent can be applied to both sides of the aluminium foil which is a positive-electrode charge collector, and the technique referred to as pressing with a roll press machine can also be used after desiccation.

[0038] [the negative electrode of 6. nonaqueous electrolyte cell] -- the configuration of a negative electrode is [that there is no limitation in any way] well-known unless it is contradictory to the principal part of the configuration of this invention, since it is not the principal part of the configuration of this invention -- it is -- it is -- the configuration of arbitration is employable.

[0039] For example, when a nonaqueous electrolyte cell is a lithium ion battery, the carbon material of arbitration, such as occlusion, easily graphitized carbon which can be emitted, difficulty graphitized carbon, and a graphitization material, can be reversibly used for a lithium ion. And at least, the mixture of these negative-electrode active materials which made a kind and the binder the shape of a paste with the partially aromatic solvent can be applied to both sides of the copper foil which is a negative-electrode charge collector, and the technique referred to as pressing with a roll press machine can also be used after desiccation.

[0040] Each configuration of a positive electrode in case the above-mentioned nonaqueous electrolyte cell is a lithium ion battery, and a negative electrode can also transpose the either to a metal lithium.

[0041] [the configuration of 7. nonaqueous electrolyte cell] -- the overall configuration of a cell is [that there is no limitation in any way] well-known unless it is contradictory to the principal part of the configuration of this invention, since it is not the principal part of the configuration of this invention -- it is -- it is -- the configuration of arbitration is employable.

[0042] For example, about a cell configuration, it can be made cylindrical, a square shape, etc. When making it a cylindrical cell, a positive electrode and a negative electrode can be made to be able to counter through a separator, and winding and the general method referred to as putting this into a cell can and pouring in the electrolytic solution can also be adopted in the shape of a cylinder.

[0043]

[Example] Next, the example of the 1st invention and the 2nd invention is explained.

[0044] [Example 1] 1.4 time mol They are 500 ppm ion-exchange distilled water, and the N and N'-dicyclohexylcarbodiimide (product made from the Wako Pure Chem industry.) to 50ml (LiPF_6 / EC+PC+DEC of one mol / L (3:1:2)) of Mitsubishi Chemical electrolytic solutions. the following and "DCC" -- saying -- in addition, it sealed into the sample bottle. Acidity in the sample electrolytic solution after leaving the three samples for 30 minutes, one day, and seven days under a room temperature, respectively 0.1 mol/L The quantum was carried out by neutralization analysis in the NaOH aqueous solution (product made from the Wako Pure Chem industry).

[0045] Although 500 ppm ion-exchange distilled water was added to the above-mentioned electrolytic solution on the other hand for the comparison About the example which was not added, DCC performed the quantum similarly.

[0046] These results are shown in a table 1. In addition, the units of the numeric value in a table 1 are millimol/L. In this example, increase in quantity of fluoric acid with time was not seen in clear relative evaluation can control generating of fluoric acid by addition of like and DCC, and moreover according to the merits and demerits of neglect time amount from a table 1.

[0047]

[A table 1]

	添加剤	放置時間		
		30分	1日	7日
実施例 1	DCC	0.5	0.4	0.7
	無し	5.8	61.3	86.3
実施例 2	DCC	1.9	1.1	1.6
実施例 3	DIC	0.4	0.9	0.5
比較例 1	BaO	7.6	55.3	73.2
比較例 2	無水酢酸	107.7	107.4	106.7

[0048] [Example 2] It can set in the example 1. In the addition of DCC, 500 ppm ion-exchange distilled water is received. It carried out on the same conditions as an example 1 except [all] the point changed into the mol 0.3 times. More nearly too than the result shown in a table 1 Generating of fluoric acid could be controlled by addition of DCC, and, moreover, increase in quantity of fluoric acid with time was not seen in relative evaluation by the merits and demerits of neglect time amount.

[0049] [an example 3] -- it replaces with DCC in an example 1 -- an N and N'-diisopropyl carbodiimide (product made from the Wako Pure Chem industry.) the following and "DIC" -- saying -- It carried out on the same conditions as an example 1 except [all] the point which carried out equimolecular amount addition with DCC. From the result shown in a table 1, generating of fluoric acid could be controlled by addition of DIC, and, moreover, increase in quantity of fluoric acid with time was not seen in relative evaluation by the merits and demerits of neglect time amount.

[0050] [Example 1 of a comparison] The fluoric acid depressor effect of the metallic oxide in invention given in JP,4-284372,A was retested. That is, it can set in the example 1. It replaces with DCC and is the electrolytic solution. Suspension of 0.5% of the weight of the BaO (product made from the Wako Pure Chem industry) was carried out, and all other points were performed on the same conditions as an example 1. From the result shown in a table 1, generating of fluoric acid could not be controlled by addition of BaO, and an effect was not accepted.

[0051] [Example 2 of a comparison] The acid depressor effect of the acid anhydride in invention given in JP,7-122297,A was retested. That is, it can set in the example 1. It replaced with DCC, the acetic anhydride (product made from the Wako Pure Chem industry) of this and an equimolecular amount was added, and all other points were performed on the same conditions as an example 1. From the result shown in a table 1, generating of an acid could not be controlled by addition of an acetic anhydride, and an effect was not accepted. It is thought that this result is because the acetic acid was generated instead although possibly generating of fluoric acid was controlled.

[0052] [Example 4] The LiMn₂O₄ 18.5 (product made from Mitsui Mining & Smelting industry) weight section, and acetylene black (Tokai Carbon make) The 1.5 weight-sections and polyvinylidene fluoride powder (product made from KUREHA chemistry) The slurry was obtained by mixing enough 8 weight sections and the N-methyl pyrrolidone (product made from Wako Pure Chem industry) 72 weight section.

[0053] An applicator is used for this slurry and it is 20 micrometers in thickness. It applies on aluminum foil (positive-electrode charge collector), a desiccation press is carried out, and it is to both sides. LiMn₂O₄ Applied thickness 160 micrometers The positive-electrode material was obtained.

[0054] On the other hand, it is a graphite (Osaka Gas MCMB). It is N-methyl pyrrolidone about the polyvinylidene fluoride powder 10 weight section to the 100 weight sections. Solution which dissolved in the 100 weight sections The slurry was obtained by mixing the 100 weight sections enough. An applicator is used for this slurry and it is 10 micrometers in thickness. Thickness which applied on copper foil (negative-electrode charge collector), carried out the desiccation press, and applied the carbon material to both sides 100 micrometers The negative-electrode material was obtained.

[0055] And what pierced to the negative electrode what pierced to the positive electrode what pierced the above-mentioned positive-electrode material to discoid with a diameter of 15mm, and pierced the above-mentioned negative-electrode material to discoid with a diameter of 17mm, and pierced the polyethylene separator (Tonen

Chemical make) to discoid with a diameter of 19.5mm further was used for the separator, and the coin mold cell which the positive electrode and the negative electrode were made to counter through a separator was created.

[0056] the above-mentioned cell -- as the electrolytic solution -- Mitsubishi Chemical 1 mol/L LiPF₆ / EC+DEC (1:1) -- 500 ppm of ion-exchange distilled water -- the -- 1.4 time mol What added DCC and was heated by 60-degreeC for 96 hours was poured in. And it ****(ed) and considered as the prototype cell of this example.

[0057] It is 1 mA/cm² about this above-mentioned example and the prototype cell for a comparison. Cell voltage by the constant current constant voltage It charges until it is set to 4.2V (the charging time is 6 hours), and it continues. 0.5 mA/cm² Cell voltage by constant current The cycle deterioration test was performed by repeating this by making into 1 cycle ** and the discharge process referred to as discharging until it is set to 3.0V.

[0058] the result is as being shown in drawing 1 -- it turns out that the cycle property of a cell has been remarkably improved by addition of DCC.

[0059] [Example 5] It can set in the example 4. For the example of DCC addition, and a comparison Ion-exchange distilled water added to the electrolytic solution about the non-adding example of DCC Except [all] the point made 1500 ppm increase the quantity of, the cell was made as an experiment on the same conditions, and the cycle deterioration test was performed.

[0060] as the result being shown in drawing 2 -- it is -- too -- The cycle property of a cell is remarkably improved by addition of DCC. Furthermore, it compares with this example and is the example 4 with few additions of water. Even if it compares with the example of DCC addition, it turns out that it is equal.

[0061] [an example 6] -- the carbon material positive electrode (thing of the same configuration as the negative electrode of an example 4) pierced to discoid with a diameter of 15mm and the negative electrode of the metal lithium (wood formation make) pierced to discoid with a diameter of 17mm are used -- addition of DCC It was referred to as 3.6 millimol /L, and other points made the same cell as an example 4 as an experiment. Apart from this, the same prototype cell for a comparison was also constituted except the point of not adding DCC.

[0062] The charge and discharge test was performed about this above-mentioned example and the prototype cell for a comparison. Charge conditions 0.5 mA/cm² It is termination voltage by constant-current charge. It is referred to as 1.5V, and they are discharge conditions. 0.5 mA/cm² Termination voltage was set to 0V by constant-current discharge. the result is as being shown in drawing 3 -- it turns out that the capacity of a cell has been remarkably improved by addition of DCC.

[0063] [Example 7] It can set in the example 4. For the example of DCC addition, and a comparison It is attached to the non-adding example of DCC, and is the electrolytic solution 1 mol/L made from the Toyama pharmaceutical industry Except [all] having changed to LiBF₄ / EC+DEC (1:1), the cell was made as an experiment on the same conditions, and the cycle deterioration test was performed.

[0064] the result is as being shown in drawing 4 -- the cycle property of a cell is effectively improved by addition of DCC. In the case of the electrolytic solution which used LiBF₄ for the supporting electrolyte from this It turned out that addition of DCC is effective.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing ** and the discharge cycle property of the example of this invention, and the example of a comparison.

[Drawing 2] It is drawing showing ** and the discharge cycle property of the example of this invention, and the example of a comparison.

[Drawing 3] It is drawing showing the cell capacity of the example of this invention, and the example of a comparison.

[Drawing 4] It is drawing showing ** and the discharge cycle property of the example of this invention, and the example of a comparison.

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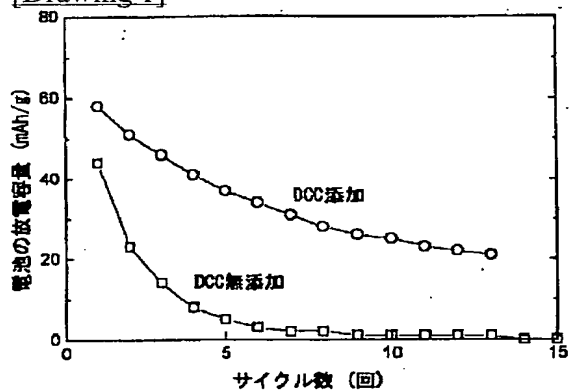
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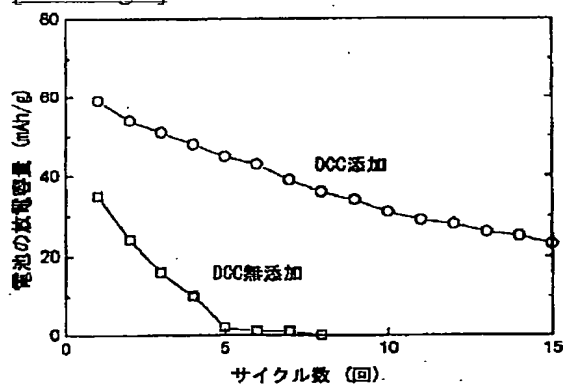
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DRAWINGS

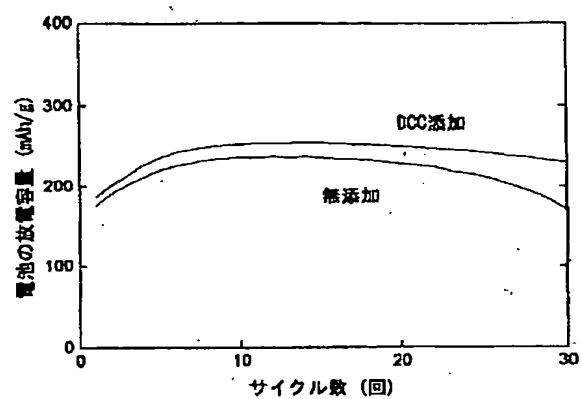
[Drawing 1]



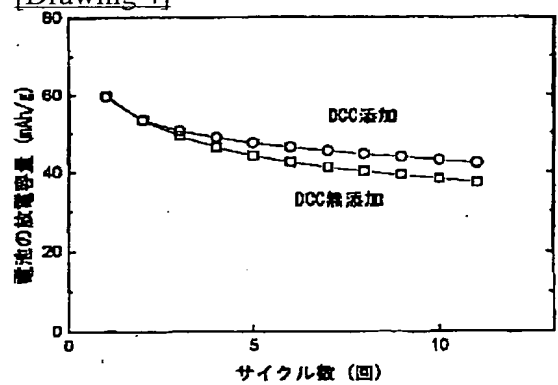
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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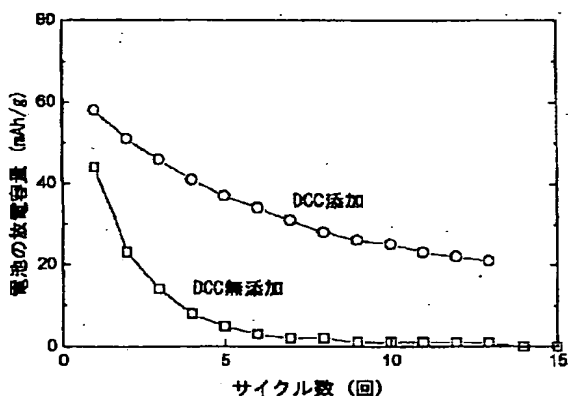
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(54) 【発明の名称】 電池用非水電解液及び非水電解液電池

(57) 【要約】

【目的】 非水電解液電池において、水の混入に基づくハロゲン酸の発生を防止して、電池の劣化を防ぐ。

【構成】 氷との反応によりハロゲン酸を生じ得る支持電解質を含む電池用非水電解液又はこれを用いた非水電解液電池において、水をトラップして安定で無害な錯体を生成する錯体形成化合物を添加する。



【特許請求の範囲】

【請求項1】 水と反応してハロゲン酸を生じ得る支持電解質を含む非水電解液に、前記水及び支持電解質と相互作用して不活性な錯体を形成することによりハロゲン酸を生じさせない錯体形成化合物を添加したことを特徴とする電池用非水電解液。

【請求項2】 少なくとも正／負極のいずれかの活物質としてリチウム又はその化合物を含み、かつ、請求項1に記載の電池用非水電解液を用いることを特徴とする非水電解液電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、電池用非水電解液及び非水電解液電池に関し、更に詳しくは、例えば一定のハロゲン化合物等を支持電解質とした非水電解液を用いるリチウム二次電池等において、不可避免的に介在し得る少量の水分に起因してハロゲン酸が発生することへの対策を講じた電池用非水電解液、及びこれを用いた非水電解液電池に関する。

【0002】

【従来の技術】リチウム又はその化合物を電極活物質に用い、そのことから電解液として支持電解質を含む有機溶媒を利用する非水電解液電池が、例えば電子部品用小型電源としての一次電池や、電気自動車のバッテリー用等に向けられる二次電池あるいはリチウムイオン電池等としてその有用性を注目されている。

【0003】これらの非水電解液電池において、上記の支持電解質には、例えばハロゲン化合物である LiPF_6 等が良く用いられているが、非水である筈の電解液中に若干の水分が不可避免的に混入していたり、あるいは他の電池材料からの吸着により生じた水分が存在していたりすると、次の「化1」に示すような反応が起こり、フッ化水素HFのごときハロゲン酸が発生させる。

【0004】

【化1】



【0005】フッ化水素は電池構成材料を劣化させ、更に電池性能を劣化させると言う問題がある。更に、前記「化1」の反応は高温域で促進されることが知られている。このため、例えば、 $-30^\circ\text{C} \sim 60^\circ\text{C}$ の温度域での安定的動作が要求される電気自動車のバッテリー用二次電池においては特に問題が顕著となり、 LiPF_6 を支持電解質とする非水電解液電池は適用が困難であるとされている。

【0006】そしてこの問題を解決するため、従来、次のような提案がされている。例えば特開平4-284372号公報に記載された非水電解液二次電池の発明においては、 LiPF_6 を支持電解質とする非水電解液に対し、 Al_2O_3 、 MgO 、 BaO から選ばれる酸化物を添加することにより、これらの酸化物が電解液に生じたフッ化

水素を吸着し、反応系外へ除去する、としている。

【0007】又、特開平7-122297号公報に記載された非水電解液電池の発明においては、 LiPF_6 を支持電解質とする非水電解液に対し、酸無水物（例えば、無水酢酸）を添加することにより、これらの酸無水物が電解液中の水を予め捕捉して、前記「化1」の反応を抑制する、としている。

【0008】

【発明が解決しようとする課題】しかし、前記特開平4-284372号公報に記載の発明については、本件発明者の追試によれば、電池として現実的に許容し得る添加量の酸化物によっては、フッ化水素の除去は極めてゆっくりと進行するため、フッ化水素の発生速度に追いつかない。従って、フッ化水素による電池の劣化等を有効に防止するに至らない、と言う問題がある。

【0009】一方、前記特開平7-122297号公報に記載の発明については、酸無水物による脱水効果は高いが、その結果、酸無水物に起因する酸が発生することになり、いわば、ハロゲン酸を他の酸に置換するだけのことである。そしてハロゲン酸に対して例えば酢酸等は相対的に弱酸であるとは言え、やはり電解液や電池缶材料の劣化をもたらすことになりはなく、本質的な解決になっていない。

【0010】そこで本発明では、水と反応してハロゲン酸を生じ得る支持電解質を含む電池用の非水電解液、又はこれを用いた非水電解液電池において、ハロゲン酸による弊害を有効に防止し、しかも上記従来技術のような二次的な問題も生じさせないことを、その解決すべき技術的課題とする。

【0011】

【着眼点】本件発明者は、ハロゲン酸の発生原因となる水分を、無害でかつ反応速度の大きい錯体形成反応によって封じ込めることが、上記課題の解決に有効であることに着眼した。

【0012】

【課題を解決するための手段】

【0013】（第1発明の構成）上記課題を解決するための本願第1発明（請求項1に記載の発明）の構成は、水と反応してハロゲン酸を生じ得る支持電解質を含む非水電解液に、前記水及び支持電解質と相互作用して不活性な錯体を形成することによりハロゲン酸を生じさせない錯体形成化合物を添加した電池用非水電解液である。

【0014】（第2発明の構成）上記課題を解決するための本願第2発明（請求項2に記載の発明）の構成は、少なくとも正／負極のいずれかの活物質としてリチウム又はその化合物を含み、かつ、請求項1に記載の電池用非水電解液を用いる非水電解液電池である。

【0015】

【発明の作用・効果】第1発明、第2発明において、非水電解液中に若干の水分が混入していたり、あるいは他

の電池材料からの吸着により生じた水分が存在していたりしても、これらの水分が錯体形成化合物により不活性な錯体中に封じ込められる。

【0016】平衡反応であるハロゲン酸の生成とは異なり、一般に錯体形成反応は不可逆性が強いので、前記「化1」の反応よりも錯体形成反応が優先して起こる。このため、ハロゲン酸の生成が有効に阻止される。

【0017】そして、錯体形成反応の一般的特徴として反応速度が速いため、特開平4-284372号公報に記載の発明のような反応速度の不足による不具合がなく、又、本発明においては特開平7-122297号公報に記載の発明のように二次的に他の有害物質を生ずると言う不具合もない。

【0018】以上のことから、本発明に係る電池用非水電解液あるいは非水電解液電池においては、水と反応してハロゲン酸を生じ得る支持電解質を用いているにも関わらず、非水電解液に水が混入しても、電池構成材料の劣化や電池性能の劣化が阻止される。

【0019】

【発明の実施の形態】次に、第1発明、第2発明の実施の形態について説明する。

【0020】〔1. 本発明の対象〕原則として、水と反応してハロゲン酸を生じ得る支持電解質を含む電池用非水電解液及びこれを用いた非水電解液電池は、全て本発明の対象となり得る。現在のところ、非水電解液電池は、少なくとも正/負極のいずれかの電極活物質としてリチウム又はその化合物を用いる、いわゆる「リチウム電池」が殆どを占めている。

【0021】本発明の対象であるこのようなリチウム電池の2、3の例として、負極にリチウムを用いると共に正極には二酸化マンガン、フッ化亜鉛、酸化銅あるいは塩化チオニル等を用いるリチウム乾電池（一次電池）、負極にリチウム又はその合金を含むと共に正極には活性炭、二硫化チタンあるいは二硫化モリブデン等を用いるリチウム蓄電池（二次電池）、負極にリチウムイオンを吸蔵・放出できる炭素材料を用いると共に正極にリチウム遷移金属化合物を用いるリチウムイオン電池、等を挙げることができる。

【0022】なお、上記のようなリチウム電池でなくても、前記本発明の課題が生じ得る限りにおいて、本発明の対象たる電池用非水電解液、非水電解液電池である。

【0023】〔2. 支持電解質〕支持電解質とは、電池用非水電解液において、電解液の導電率を高めて電池の充電と放電を効率的に行うと言う目的で添加された物質を言う。良く知られた支持電解質に LiPF_6 や LiBF_4 があるが、本発明ではこれらに限定されず、他にも、例えば LiAsF_6 のように、水と僅かに反応してフッ化水素のようなハロゲン酸を生じ得る支持電解質一般が含まれる。

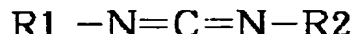
【0024】〔3. 電池用非水電解液における有機溶

媒〕支持電解質との特段のミスマッチングがない限りにおいて、有機溶媒の種類には限定がない。その2、3の例として、エチレンカーボネート（EC）、プロピレンカーボネート（PC）、ジエチルカーボネート（DEC）、ジメチルカーボネート、ジメトキシエタン、γブチロラクトン等や、これらの二種以上の混合溶媒を使用できる。

【0025】〔4. 錯体形成化合物〕本発明の錯体形成化合物は、水及び前記支持電解質と反応して不活性な錯体を形成するものを言う。その代表的なものは、次の「化2」に示すカルボジイミド化合物である。

【0026】

【化2】



【0027】上記の「化2」において、 R1 、 R2 は、それぞれ、水素原子又は炭化水素基を示し、 R1 と R2 が同一であっても良く、互いに異なっていても良い。ここに「炭化水素基」とは、飽和又は不飽和の、鎖状、分岐状あるいは環状（芳香族を含む）の炭化水素基を含む。

【0028】本発明の錯体形成化合物が「化2」に示すカルボジイミド化合物である場合には、その錯体形成メカニズムは、次のようなものである、と推測される。

【0029】即ち、カルボジイミド化合物がない場合には、 LiPF_6 のイオン解離により生じた PF_6^- 負イオンが水と反応して前記「化1」のように HF を遊離するが、カルボジイミド化合物が存在すると、ジイミド結合部 $-\text{N}=\text{C}=\text{N}-$ の二重結合部が水分子と弱く水素結合し、それらに PF_6^- 負イオンが電気的に結合した錯体が形成され、このために HF を生じさせない、と考えられる。

【0030】以上の錯体形成メカニズムにおいて、 R1 、 R2 は錯体形成に直接には関与しないが、カルボジイミド化合物の非水電解液への溶解性を確保することによって錯体の形成を容易にする、と言う働きを持つ。この理由から、炭素数が3～8のアルキル基あるいはシクロアルキル基であることが、より好ましい。その具体例として、例えば以下のものがある。

【0031】それぞれ直鎖状のプロピル基、ブチル基、ペンチル基、ヘキシル基、ヘプチル基、オクチル基、及びこれらに対する *iso*-, *sec*-, *tert*- 等の関係にある全ての構造異性体の基。

【0032】シクロヘキシル基、（シクロヘキシル）メチル基、メチル側鎖が任意の置換位置にあるメチルシクロヘキシル基、メチル側鎖が任意の置換位置にあるジメチルシクロヘキシル基あるいは（メチル）シクロヘキシル）メチル基、エチル側鎖が任意の置換位置にあるエチルシクロヘキシル基。

【0033】又、 R1 、 R2 は不飽和のフェニル基、ナフチル基、ビニル基等であっても良く、炭素数3～8以外のアルキル基あるいはシクロアルキル基であっても良

い。更にR1, R2の一方が炭素数3~8のアルキル基あるいはシクロアルキル基であって他方が不飽和のフェニル基、ナフチル基、ビニル基等や炭素数3~8以外のアルキル基あるいはシクロアルキル基もしくは水素原子であっても良い。

【0034】これらの錯体形成化合物は、単一種類のものを用いても、二種類以上のものを併用しても良い。カルボジイミド化合物は、非水電解液中の水分量が通常は約30 ppmであるという理由から、非水電解液重量に対して30 ppm以上を添加することが好ましい。逆に、電解液自体の導電率を下げるという理由から、10,000ppmを超える添加は無意味、あるいは好ましくない。

【0035】以上のような本発明の錯体形成化合物を添加する方法には限定がなく、例えば電池組付け前に非水電解液に添加しても、電池組付け後の封缶前に電池容器内に直接添加しても良い。非水電解液に添加した錯体形成化合物の分散状態には別段の限定がない。

【0036】〔5. 非水電解液電池の正極〕正極の構成は、本発明の構成の主要部ではないから、本発明の構成の主要部と矛盾しない限りにおいて、何ら限定なく公知のあるいは任意の構成を採用することができる。

【0037】例えば非水電解液電池がリチウムイオン電池である場合には、正極の活物質として LiCoO_2 、 LiNiO_2 、 LiMn_2O_4 等の少なくとも一種と、導電助剤及びバインダとを混合溶剤にてペースト状にした合剤を、正極集電体であるアルミニウム箔の両面に塗布し、乾燥後、ロールプレス機にて圧縮成形するという手法を用いることもできる。

【0038】〔6. 非水電解液電池の負極〕負極の構成は、本発明の構成の主要部ではないから、本発明の構成の主要部と矛盾しない限りにおいて、何ら限定なく公知のあるいは任意の構成を採用することができる。

【0039】例えば非水電解液電池がリチウムイオン電池である場合には、リチウムイオンを可逆的に吸蔵・放出できる易黒鉛化炭素、難黒鉛化炭素、黒鉛化材料等の任意の炭素材料を使用できる。そしてこれらの負極活物質の少なくとも一種とバインダとを混合溶剤にてペースト状にした合剤を、負極集電体である銅箔の両面に塗布し、乾燥後、ロールプレス機にて圧縮成形するという手法を用いることもできる。

【0040】上記の、非水電解液電池がリチウムイオン電池である場合における正極、負極のそれぞれの構成は、そのいずれか一方を、金属リチウムに置き換えることもできる。

【0041】〔7. 非水電解液電池の構成〕電池の全体的構成は、本発明の構成の主要部ではないから、本発明の構成の主要部と矛盾しない限りにおいて、何ら限定なく公知のあるいは任意の構成を採用することができる。

【0042】例えば電池形状については、円筒型、角型等にすることができる。円筒型電池にする場合には、正

極と負極とをセパレータを介して対向させ、円筒状に巻回し、これを電池缶に入れ電解液を注入すると言う一般的な方法を採用することもできる。

【0043】

【実施例】次に、第1発明及び第2発明の実施例について説明する。

【0044】〔実施例1〕三菱化学製の電解液(1mol/Lの $\text{LiPF}_6/\text{EC}+\text{PC}+\text{DEC}(3:1:2)$)50mlに対して、500ppmのイオン交換蒸留水と、その1.4倍モルのN,N'-ジシクロヘキシルカルボジイミド(和光純薬工業製。以下、「DCC」と言う)を加えて、サンプルびんに密封した。その試料3例を、それぞれ室温下に30分、1日、7日間放置した後、試料電解液中の酸量を0.1mol/LのNaOH水溶液(和光純薬工業製)で中和滴定法により定量した。

【0045】一方、比較のために、上記電解液に500ppmのイオン交換蒸留水を加えたがDCCは添加しなかった例についても、同様にして定量を行った。

【0046】これらの結果を表1に示す。なお、表1中の数値の単位は、ミリモル/Lである。本実施例においては、表1より明らかなように、DCCの添加によりフッ酸の発生を抑制することができ、しかも放置時間の長短による相対評価においてフッ酸の経時的増量が見られなかった。

【0047】

【表1】

	添加剤	放置時間		
		30分	1日	7日
実施例1	DCC	0.5	0.4	0.7
	無し	5.8	61.3	86.3
実施例2	DCC	1.9	1.1	1.6
実施例3	DIC	0.4	0.9	0.5
比較例1	BaO	7.6	55.3	73.2
比較例2	無水酢酸	107.7	107.4	106.7

【0048】〔実施例2〕実施例1におけるDCCの添加量を、500ppmのイオン交換蒸留水に対する0.3倍モルに変えた点以外は全て実施例1と同じ条件で行った。表1に示すその結果より、やはりDCCの添加によりフッ酸の発生を抑制することができ、しかも放置時間の長短による相対評価においてフッ酸の経時的増量が見られなかった。

【0049】〔実施例3〕実施例1におけるDCCに代えて、N,N'-ジイソプロピルカルボジイミド(和光純薬工業製。以下、「DIC」と言う)をDCCと等モル量添加した点以外は全て実施例1と同じ条件で行った。表1に示すその結果より、DICの添加によりフッ酸の発生を抑制することができ、しかも放置時間の長短による相対評価においてフッ酸の経時的増量が見られなかった。

【0050】〔比較例1〕特開平4-284372号公報に記載の発明における金属酸化物のフッ酸抑制効果を追試した。即ち、実施例1におけるDCCに代えて、電解液の0.5重量%のBaO(和光純薬工業製)を懸濁させ、その他の点は全て実施例1と同じ条件で行った。表1に示すその結果より、BaOの添加によりフッ酸の発生を抑制することができず、効果が認められなかった。

【0051】〔比較例2〕特開平7-122297号公報に記載の発明における酸無水物の酸抑制効果を追試した。即ち、実施例1におけるDCCに代えて、これと等モル量の無水酢酸(和光純薬工業製)を添加し、その他の点は全て実施例1と同じ条件で行った。表1に示すその結果より、無水酢酸の添加により酸の発生を抑制することができず、効果が認められなかった。この結果は、フッ酸の発生は抑制されたかも知れないが、代わりに酢酸が発生したためであると考えられる。

【0052】〔実施例4〕 LiMn_2O_4 (三井金属工業製)18.5重量部、アセチレンブラック(東海カーボン製)1.5重量部、ポリフッ化ビニリデン粉末(クレハ化学製)8重量部、N-メチルピロリドン(和光純薬工業製)72重量部を十分混合することにより、スラリーを得た。

【0053】このスラリーを、アブリケータを用いて厚さ20 μm のアルミ箔(正極集電体)上に塗布し、乾燥プレスして、両面に LiMn_2O_4 を塗布した厚さ160 μm の正極材料を得た。

【0054】一方、黒鉛(大阪ガス製のMCMB)100重量部に対して、ポリフッ化ビニリデン粉末10重量部をN-メチルピロリドン100重量部に溶解した溶液100重量部を十分混合することにより、スラリーを得た。このスラリーを、アブリケータを用いて厚さ10 μm の銅箔(負極集電体)上に塗布し、乾燥プレスして、両面に炭素材料を塗布した厚さ100 μm の負極材料を得た。

【0055】そして、上記正極材料を直径15mmの円盤状に打ち抜いたものを正極に、上記負極材料を直径17mmの円盤状に打ち抜いたものを負極に、更にポリエチレンセパレータ(東燃化学製)を直径19.5mmの円盤状に打ち抜いたものをセパレータに用いて、正極と負極をセパレータを介して対向させたコイン型電池を作成した。

【0056】上記電池に、電解液として、三菱化学製の1mol/Lの LiPF_6 /EC+DEC(1:1)にイオン交換蒸留水500ppmとその1.4倍モルのDCCを加えて60°Cで96時間加熱したもの、を注入した。そして封缶して本例の試作電池とした。

【0057】上記本例及び比較用の試作電池について1mA/cm²の定電流定電圧で電池電圧が4.2Vになるまで充電し(充電時間は6時間)、続いて0.5mA/cm²の定

電流で電池電圧が3.0Vになるまでの放電を行う、と言う充・放電過程を1サイクルとして、これを繰り返すことによりサイクル劣化試験を行った。

【0058】その結果は図1に示す通りであり、DCCの添加によって電池のサイクル特性が著しく改善されたことが分かる。

【0059】〔実施例5〕実施例4におけるDCC添加例と、比較用のDCC非添加例とにつき、電解液に加えるイオン交換蒸留水を1500ppmに増量させた点以外は全て同じ条件で電池を試作し、サイクル劣化試験を行った。

【0060】その結果は図2に示す通りであり、やはりDCCの添加によって電池のサイクル特性が著しく改善されている。更に、本例に比べて水の添加量が少ない実施例4のDCC添加例と比較しても、遜色がないことが分かる。

【0061】〔実施例6〕直径15mmの円盤状に打ち抜いた炭素材料正極(実施例4の負極と同じ構成のもの)と、直径17mmの円盤状に打ち抜いた金属リチウム(林化成製)の負極を用い、DCCの添加量を3.6ミリモル/Lとして、その他の点は実施例4と同一である電池を試作した。これとは別に、DCCを加えない点以外は同一である比較用の試作電池も構成した。

【0062】上記本例及び比較用の試作電池について充放電試験を行った。充電条件を0.5mA/cm²の定電流充電で終止電圧を1.5Vとし、又、放電条件は0.5mA/cm²の定電流放電で終止電圧を0Vとした。その結果は図3に示す通りであり、DCCの添加によって電池の容量が著しく改善されたことが分かる。

【0063】〔実施例7〕実施例4におけるDCC添加例と比較用のDCC非添加例とにつき、電解液を富山薬品工業製の1mol/Lの LiBF_4 /EC+DEC(1:1)に替えた以外は全て同じ条件で電池を試作し、サイクル劣化試験を行った。

【0064】その結果は図4に示す通りであり、DCCの添加により電池のサイクル特性が効果的に改善されている。このことから、 LiBF_4 を支持電解質に用いた電解液の場合でもDCCの添加が有効であることが分かった。

【図面の簡単な説明】

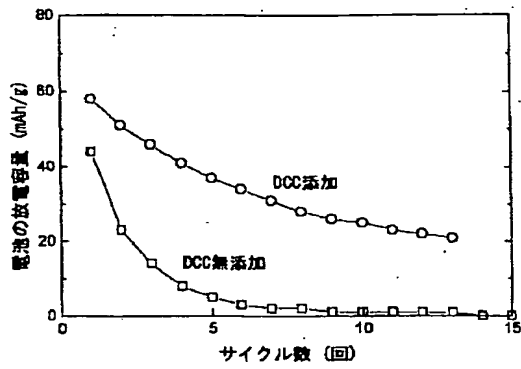
【図1】本発明例及び比較例の充・放電サイクル特性を示す図である。

【図2】本発明例及び比較例の充・放電サイクル特性を示す図である。

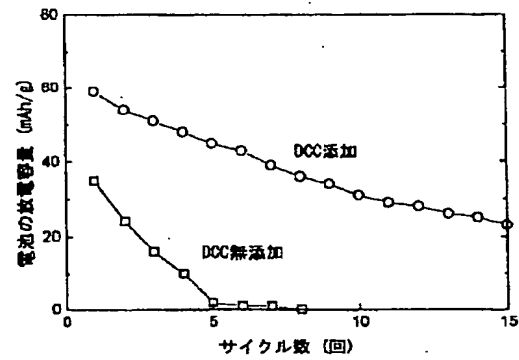
【図3】本発明例及び比較例の電池容量を示す図である。

【図4】本発明例及び比較例の充・放電サイクル特性を示す図である。

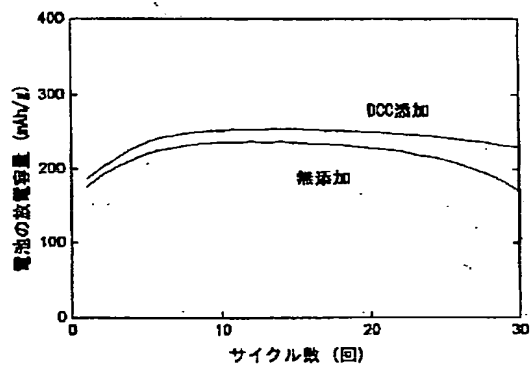
【図1】



【図2】



【図3】



【図4】

